



Exploring the effect of additives on polyamide membrane surface for seawater desalination using density functional tools



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HIGHLIGHTS

- Polyamide membrane surface modified with various additives is investigated.
- Binding of metal ions to the surface is favored by polar functional groups.
- Additives with carboxylate and phosphate groups show greater binding.
- TRP and AMP bound polyamide is proposed as an effectual membrane surface.

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ABSTRACT

The efficiency of certain additives like tryptophan (TRP), adenosine monophosphate (AMP) and phenethylamine (PEA) on polyamide membrane (PA) surface for better salt rejection is studied through density functional theory. The interaction energies of monovalent (Na^+ , K^+) and divalent (Ca^{2+} , Mg^{2+}) cations with pure PA and modified PA surfaces are calculated and a stronger binding of divalent cations over monovalent cations is noticed. The increasing order of binding of PA surfaces with metal-ions is $\text{PA_PEA} < \text{PA} < \text{PA_AMP} < \text{PA_TRP}$. The two major factors influencing the binding of metal ions to the surfaces are cation- π interactions between the metal ion and the π -cloud of the additive and the nucleophilic character of the membrane surface. The increasing order of metal ion binding to any of the PA surface is $\text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$. Both gas phase and solvent phase interaction energies follow the same trend of metal ion binding to the PA surface. The findings from the interaction studies are supported by conceptual density functional descriptors. TRP and AMP bound PA surfaces with polar functional groups are relatively presented as an effectual membrane surface for salt rejection than the pure polyamide surface.

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1. Introduction

Explosive population growth, rapid urbanization, pollution of natural sources of water and environmental impact have resulted in inadequate access to drinking water for a large percentage of population across the globe. One of the most challenging problems for engineers and scientists is to make quality water available for the entire human society at an affordable cost. In this regard, desalination, the process of removing salt from seawater, has gained utmost importance during the last few decades. Reverse osmosis (RO) process has become the method used by several large scale desalination plants around the globe, which involves a semi-permeable membrane to separate salts from seawater. The most common membrane used is polyamide

based thin-film composite membrane (TFC), which is produced by an interfacial polymerization process. In recent years, although the cost of RO process in desalination has been reduced substantially it is still quite expensive for economic widespread use and has huge impact on the environment [1,2]. With this regard, forward osmosis (FO) process evolved as an alternative, however, with less number of large scale plants than the RO process. The two components that play a major role in the FO process are the membrane and the draw solute. The quest for novel materials for water treatment facilities especially RO and FO, has paved the way towards innovation in material and design of desalination processes [3].

A steady increase is observed in the application of molecular dynamics (MD) simulations for addressing issues related to membrane desalination. Studies on water and salt transport in the FT30 reverse osmosis membrane shows that water transport occurs by a “jump” diffusion process and its mobility decreases with an increase in density of the polymer matrix [4,5]. A heuristic approach to build the polymer membrane is developed [6] based on distance criteria for amide bond

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formation and later employed by other authors [7] to build a realistic atomistic model of the membrane which has been used for MD simulations. The properties of RO membrane, FT30, were investigated using fully atomistic MD simulations [8–10] and a high degree of variability in the resistance to salt diffusion inside the membrane is noted. This is attributed to the structure of water encountered by the salt ions as they permeate through the membrane. Recently [11], the interaction of alginate foulants with hydrated PA membrane through MD simulations is explored. In addition to these, computational techniques have been used to propose novel materials like carbon nanotubes [12,13], purely siliceous zeolites [14], nanoporous graphene [15,16], boron nitride nanotubes [17], hydrophilic FAU and hydrophobic MFI zeolites [18] for RO process. Very recent work by the authors shows through MD simulations and experiments that incorporation of inorganic nanoparticle like POSS (polyoctahedral oligomeric silsesquioxanes) into the PA membrane increases the water flux and salt rejection compared to pure PA membranes [19].

Compared to MD simulations, studies employing first principles or density functional theory (DFT) related to membrane research are scarce. DFT with its ability to treat systems of larger size and greater degree of accuracy in a systematic fashion makes it an ideal tool for the present context. A study on interaction between natural organic matter and fully/semi-aromatic polyamide based membranes shows that organic molecules with carboxylic group adsorb better than phenolic and acetic acid groups on fully aromatic polyamide membrane [20]. A recent study [21] examined the salt rejection behavior of primary and secondary diamines in reaction with TMC. The authors use conceptual DFT to calculate parameters like hardness, global softness, chemical potential, Fukui functions, nucleophilicity and conclude that piperazine based TFC membrane is better for rejection of bivalent ions than the *m*-phenylene diamine (MPD) based membranes.

Several studies have focused on modification of the chemical structure of monomers (MPD,TMC) by functional group substitution for high permeability and better salt rejection [22–29]. For example, disulfonated diamine is used as a monomer instead of MPD and the resulting new membrane is found to have a higher permeate flux and reduced chlorine tolerance compared to membranes based on MPD and TMC [22]. Improvements in resistance to chlorine is found [24] when TFC membrane is prepared with *m*-phenylenediamine-4-methyl (MMPD) and cyclohexane-1,3,5-tricarbonyl chloride (HTC) as monomers. In a similar way there are several studies [25–29] which use various monomers to prepare membranes through interfacial polymerization and analyze the membrane performance in terms of water flux, salt rejection, resistance to chlorine, anti-fouling properties and hydrophilicity. The alternative way, as mentioned earlier, is by incorporating nano-particles like PA-silica [30], PA-zeolite [31], PA-CNT [32,33], into the active surface of TFC membrane for better performance.

In addition, several patents focus on the development of TFC RO membranes by including various organic materials during the interfacial polymerization [34–39]. The water flux and salt rejection are shown to improve in the presence of an additional monomer comprising of an aromatic moiety, a single carboxylic acid and a single amine reactive functional group during the interfacial polymerization [36]. Some of the monomers used are 3- or 4-carboxy benzoylchloride and 3- or 4-carboxy phthalic anhydride [36]. Likewise, polymerization in the presence of an alkali metal hydroxide and an organic acid preferably with sulfo or carboxyl group results in a membrane with better permeate flux and salt rejection [37]. However, the effect of these additional monomers with specific structural characteristics is not clear. TRP and AMP have experimentally been screened in various chemicals with carboxylic or phosphorous moieties [35–37]. And it is more important to disperse and bind these chemicals inside the PA separation surface than to attach these on the surface of PA. The aromatic monomers are known to form aggregates in solution through intermolecular π - π interactions and hydrogen bonds [40]. The presence of polar functional groups is shown to disrupt the donor-acceptor interactions and the

values of their Hildebrand solubility parameters are in the range between 18 and 24 MPa^{1/2} to disorder the π - π and polar bonding interactions between the aromatic monomers [40].

Considering these structural characteristics, in the present work several organic molecules comprising an aromatic moiety and polar functional group as new additive candidates – tryptophan (TRP), adenosine monophosphate (AMP) and phenethylamine (PEA) are selected. Herein, the focus is on the effect of these additives in the polyamide membrane and their interactions with metal ions (Na^+ , K^+ , Ca^{2+} and Mg^{2+}). Density functional tools are employed to address the following: i) the interaction energies between the metal cations and pure PA, and PA bonded with additives (PA_TRP, PA_AMP and PA_PEA) surfaces, and ii) the reactivity differences between pure PA membrane and additives incorporated PA membranes using parameters like global softness, hardness, chemical potential and Fukui functions. The results show DFT as an effective tool to predict the efficiency of an additive onto a membrane surface and the subsequent change in the membrane's primary properties.

2. Computational details

The interaction of salt ions (monovalent = Na^+ , K^+ and divalent = Ca^{2+} , Mg^{2+}) with the polyamide surface in the presence and absence of additives like tryptophan (TRP), adenosine monophosphate (AMP) and phenethylamine (PEA) are studied using density functional theory. All the structures were modeled using Avogadro [41] and the cartesian coordinates are exported to Gaussian 09 [42] for geometry optimization. Becke's three parameter hybrid functional [43] is used in combination with Lee, Yang and Parr correlation formula (B3LYP) [44]. Use of this functional for similar studies is extensively addressed in the literature and widely accepted [45–48]. All the structures were optimized at the B3LYP/6–31 + G (d,p) level of theory in the gas phase with no geometry constraints. Vibrational frequencies were carried out on the optimized structures at the same level of theory to confirm for minima on the potential energy surface. In addition, we also tested the influence of solvent phase in the calculations, as in reality the experiments involve seawater for desalination. The conductor-like polarizable continuum model, CPCM, as implemented in G09 is used with water as the solvent [49]. Considering the expense of these calculations, we limited our solvent phase studies to interactions between the pure polyamide surface and metal ions. The interaction energies mentioned in the text are the relative free energies in the gas phase unless otherwise mentioned. The comparison of gas and solvent phase interaction energies for the pure PA surface is discussed in Section (3.2.6) and the importance of solvent phase is stated.

The interaction energies are calculated using the formula given below:

$$\Delta G_{\text{interaction energies}} = \left\{ \left(G_{\text{PA-M surface}} \right) - \left(G_{\text{PA surface}} + G_{\text{M ion}} \right) \right\} \quad (1)$$

where $G_{\text{PA-M surface}}$ represents the free energies of PA surface (pure or modified) with metal ions, $G_{\text{PA surface}}$ the free energy of only the PA surface and $G_{\text{M ion}}$ that of the metal ion.

2.1. Molecular models

Fig. 1 shows the structures of the monomers and additives considered in the present study. MPD and TMC are the monomers commonly used for the TFC membrane formation. The polyamide surface modeled in the present study is the smallest model formed by the reaction of one MPD and TMC. The main objective of the present study being the examination of the effect of additives on the polyamide surface and its binding towards metal ions; the present model of PA ought to be appropriate. The additives – TRP, AMP and PEA are modeled without any alterations to their original structure and therefore, TRP and AMP have

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